Interface effects on $H_2$ adsorption and dissociation on gold clusters supported on the rutile $TiO_2(110)$ surface

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Gold nanoparticles demonstrate their great potential as an effective catalyst for hydrogenation reactions. However, mechanisms of such catalytic reactions are largely not understood. In the present work we focus on the elucidation of mechanisms of $H_2$ activation and dissociation on the small free and supported gold clusters. It is demonstrated that adsorption of $H_2$ on gold clusters depends on cluster size, geometry structure, cluster flexibility and interaction with the support. In particular the role of the rutile $TiO_2(110)$ surface in the processes of $H_2$ adsorption and dissociation on the supported gold clusters is discussed.

We introduce a global reaction route mapping (GRRM) approach to find chemical bond activation pathways catalyzed by small free gold clusters $Au_n$ ($n=1–11$) with the use of anharmonic downward distortion following (ADDF) and artificial force induced reaction (AFIR) methods [1-3]. The calculations have been performed as follows: (1) automated search for isomers of free gold clusters by ADDF method; (2) physical and chemical adsorption of $H_2$ on the obtained gold clusters by AFIR method; (3) refining the obtained AFIR paths to find transition states (TSs) for $H-H$ bond dissociation. All calculations are carried out using density-functional theory (DFT) with the PBE gradient-corrected exchange–correlation functional [4]. The results of our calculations demonstrate that $H_2$ molecule prefers to bind to the low-coordinated gold atoms on the most stable cluster isomer. However, in that case the barrier for $H_2$ dissociation can be relatively high. On the other hand in GRRM approach both the global minimum (GM) and several local minima (LM) are considered simultaneously on the basis of ADDF and AFIR methods. Such approach allows one to reduce considerably the barriers for $H_2$ dissociation, as it is shown in Figure 1.

![Figure 1](image-url)

**Figure 1.** Binding energy of $H_2$ adsorbed on $Au_n$ clusters as a function of cluster size (left); activation energy for $H_2$ dissociation obtained with the use of the traditional strategy (triangles) and GRRM approach (dots) as a function of cluster size (right).
It is well known that the support material can play an important role in the catalytic processes, considerably influencing the chemical reactivity of the supported clusters [5]. Thus, recently it was demonstrated experimentally that the perimeter interface between the cluster and the support material can play the role of active sites for hydrogen dissociation by gold nanoparticles on TiO$_2$ support [6]. Therefore we have performed theoretical calculations of adsorption and dissociation of H$_2$ molecule on the gold clusters supported on the rutile TiO$_2$(110) surface [7]. We have demonstrated that TiO$_2$ (110) support considerably affects geometry structure of the supported gold clusters and promotes adsorption and dissociation of H$_2$ on Au$_n$/TiO$_2$. In particular, formation of the OH group near the supported gold cluster is an important condition for H$_2$ dissociation, as it is shown in Figure 2. The active sites for H$_2$ dissociation are located in the vicinity of the low coordinated oxygen atoms on the rutile TiO$_2$(110) surface [7]. This, combination (interplay) of several factors such as geometry structure, cluster dimensionality, presence of the low coordinated oxygen atoms in the vicinity of the cluster-surface interface, etc. are important for H$_2$ dissociation.

Figure 2. Optimized geometries in the case of (a) molecular adsorption of H$_2$ on Au$_8$(2D)/TiO$_2$, $E_b = 23$ kJ/mol; dissociative adsorption of H$_2$ on Au$_2$(2D)/TiO$_2$: (b) dissociation of H$_2$ on supported Au$_2$(2D), $E_b = 72$ kJ/mol; (c) dissociation of H$_2$ with formation of the OH group on O(2) bridge atom, $E_b = 150$ kJ/mol. Optimized geometries in the case of (d) molecular adsorption of H$_2$ on Au$_8$(3D)/TiO$_2$, $E_b = 9$ kJ/mol; dissociative adsorption of H$_2$ on Au$_2$(3D)/TiO$_2$: (e) dissociation of H$_2$ on supported Au$_2$(3D), $E_b = 53$ kJ/mol; (f) dissociation of H$_2$ with formation of the OH group on O(2) bridge atom, $E_b = 92$ kJ/mol.

References